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기계적 합금화에 의한 Iron-Silicide의 제조 및 특성

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Processing and Properties of Mechanically Alloyed Iron-Silicide

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초 록 기계적 합금화 공정을 이용하여 열전재료 $FeSi_2$ 분말을 제조하여 열간압축법을 사용하여 성형하였다. 열간압축 성형된 $FeSi_2$는 열전특성을 나타내는 β-$FeSi_2$ 상 및 상변태가 완료되지 않은 α-Fe_2Si_5와 ε-FeSi의 혼합상으로 이루어져 있음이 확인되었다. 열전재료로의 β-$FeSi_2$ 상변태 유도를 위해 항온열처리를 행하여 상변태 조건을 조사하였다. SEM, TEM, XRD, DTA 등을 이용하여 상변태 거동을 분석한 결과, 830℃에서 24시간 진공 항온열처리 후 단상의 β-$FeSi_2$ 상을 얻을 수 있었다. 항온열처리 전의 열간압축 성형체와 상변태가 완료된 β-$FeSi_2$의 기계적 성질과 열전 특성을 측정하여 비교 분석하였다.

Abstract Iron-silicide has been produced by mechanical alloying process and consolidated by hot pressing. As-consolidated iron silicides were consisted of β-$FeSi_2$ phase, and untransformed mixture of α-Fe_2Si_5 and ε-FeSi phases. Isothermal annealing has been carried out to induce the transformation to a thermoelectric semiconducting β-$FeSi_2$ phase. The condition for β-$FeSi_2$ transformation was investigated by utilizing DTA, SEM, TEM and XRD analysis. The phase transformation was shown to be taken place by a vacuum isothermal annealing at 830℃ for 24 hours. The mechanical and thermoelectric properties of β-$FeSi_2$ materials before and after isothermal annealing were characterized in this study.

Key words : Iron silicide, mechanical alloying, hot pressing, thermoelectric.

1. Introduction

Iron silicide has a great potential for thermoelectric energy conversion devices utilizing simple temperature difference effectively at medium temperature range (500~900K) without additional driving mechanisms.[1,2] The high temperature phase of iron silicide is a eutectic structure consisting of tetragonal α-Fe_2Si_5 and cubic ε-FeSi, and low temperature phase is orthorhombic β-$FeSi_2$ which is known to be an intrinsic semiconducting phase.[1~4] The β-$FeSi_2$, which is of our interests, have received great attention in a thermoelectric material because of its relatively low cost, the possibility of the improved thermoelectric efficiency, the thermal stability at high temperature and a chemical stability.[4~7] However, the conventional ingot iron-silicide is composed of α-Fe_2Si_5, which is known as α-$FeSi_2$, and cubic ε-FeSi, at even low temperature due to the slower cooling rate and the phases can not be engaged in thermoelectric application.[6] Thus, certain isothermal annealing is thought to be inevitable to induce a peritectoid reaction from α and ε phases to β phase. It is well known that extrinsic thermoelectric $FeSi_2$ can be prepared by doping Mn or Al for p-type and Co for n-type.[8,9] However, the conventional ingot technology could not allow inherently to produce homogeneous dopant distribution in the matrix.

In an effort to produce fine grain size, which might provide short diffusion path to enhance phase transformation and phase homogenization, mechanical alloying (MA) of elemental Fe and Si powders is considered in this study. The MA is known as a unique technique for solid state alloying process[10], by which alloying proceeds with consecutive cold welding and fracturing, resulting in fine grain size and phase homogenization. Non-equilibrium phases such as supersaturated solid solution, metastable intermetallic compound, amorphous phase can be synthesized by MA. It is also reported that MA materials having a fine grain size may improve thermoelectric conversion efficiency by the reduction in lattice thermal conductivity.[11] In this work, MA followed by hot pressing have been conducted in the Fe-Si system near the composition of $FeSi_2$. The effect of milling time, hot pressing and heat treatment condition on

the formation of $FeSi_2$ phase was investigated in this study. Thermoelectric and mechanical properties of β-$FeSi_2$ doped with Co (n-type semiconductor) prepared from MA process were presented, discussed and contrasted with the results of analogous studies of the conventionally processed counterparts.

2. Experimental Procedure

Appropriate elemental powder mixtures of -325 mesh Fe(99.9%), -200 mesh Si(99.9%), and -200 mesh Co(99.9%) as an n-type dopant designed to yield $Fe_{0.98}Co_{0.02}Si_2$ were mechanically alloyed by high energy attrition milling for 100 hours under an Ar atmosphere. Each charge of 100 g powder mixtures and 5 ㎜ diameter stainless steel balls were charged into a Union-type attrition mill with a weight ratio of balls to powder of about 20 to 1. As-milled powders were sieved to -325 mesh to discard unalloyed or partially alloyed portions, which usually existed in large particles.[12] After degassing in vacuum at 400 ℃ for 2 hours, The powder was hot pressed in a cylindrical high strength graphite die with an internal diameter of 25.4 ㎜. The hot pressing operation was carried out under vacuum with a stress of 35 MPa at 1000 ℃ for 2 hours.

In order to investigate the degree of alloy during milling, consolidation and isothermal annealing, X-ray diffraction(XRD) analysis was carried out in MA powders, as-consolidated and heat treated specimen. Since iron-silicides are generally composed of α-Fe_2Si_5 and ε-FeSi at even low temperature due to the slower cooling rate and difficult to induce peritectoid transformation, a differential thermal analysis(DTA) was engaged to determine transformation temperature with the relatively slower heating and cooling rates. For DTA analysis, MA powders, hot pressed specimens were heated with 60 ℃/min up to 800 ℃ and then heated with 3 ℃/min up to 1100 ℃ in an Ar atmosphere. The cooling cycle was done with the same rate.

SEM and TEM were employed for the observation and identification of phases and microstructures. Microhardness was measured and the cracks around indentation were also measured to characterize general mechanical properties of hot pressed specimen. Electrical conductivity(σ) and Seebeck coefficient(α) were measured in the hot pressed specimens before and after isothermal annealing, and the thermoelectric power factor(θ) values were also evaluated and compared with those of counterparts. Electron mobility(μ) and concentration(n) were also obtained by Hall coefficient(RH) measurement.

3. Results and Discussion

Nominal composition of $Fe_{0.98}Co_{0.02}Si_2$ (n-type iron silicide) powders have been produced by mechanical alloying process in a controlled atmosphere using high energy attrition mill for 100 hours. The MA powders were sieved to 325 mesh to avoid the residual unalloyed portion which usually come from larger particles.[12] As-sieved powder size was typically from 3 to 6㎛, and the morphology was generally spherical as shown in Fig. 1. Though the compositions were slightly off stoichiometry, all batches were within ±1% of the designed composition. A typical chemical composition of MAed powders produced was 67.12 at.% of Si, 32.23 at.% of Fe, and 0.65 at.% of Co.

The powders were successfully consolidated by vacu-

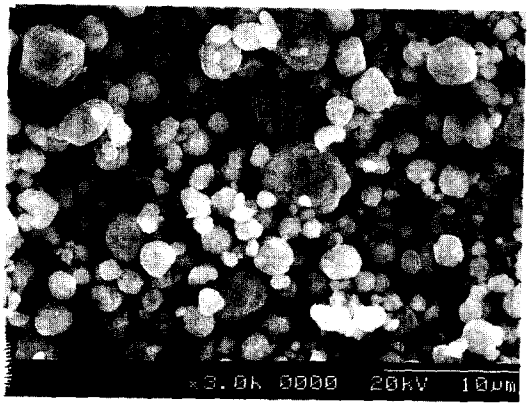

Fig. 1. SEM micrograph of the $Fe_{0.98}Co_{0.02}Si_2$ powder, mechanically alloyed for 100 hours.

Table 1. Thermoelectric and electronic transport properties of the vacuum hot pressed(VHPed) and isothermal annealed $Fe_{0.98}Co_{0.02}Si_2$.

Parameters	VHPed	Annealed
Electrical conductivity, σ ($\Omega^{-1}cm^{-1}$)	1.13×10^{2}	1.01×10
Seebeck coefficient, α (μV/K)	-13.7	-216.1
Thermoelectric power factor θ (nW/㎝K^2)	2.12×10	4.72×10^{2}
Hall coefficient, R_H (cm^3/C)	-1.65×10^{2}	-3.72
Electron mobility, μ (cm^2/Vsec)	1.86×10^{4}	3.75×10
Electron concentration, n (cm^{-3})	3.78×10^{16}	1.68×10^{18}

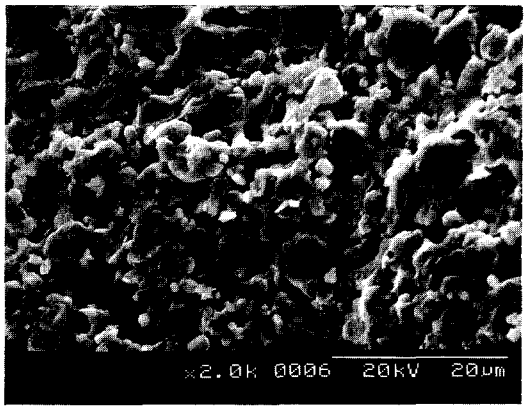

Fig. 2. SEM micrograph of vacuum hot pressed $Fe_{0.98}Co_{0.02}Si_2$ microstructure.

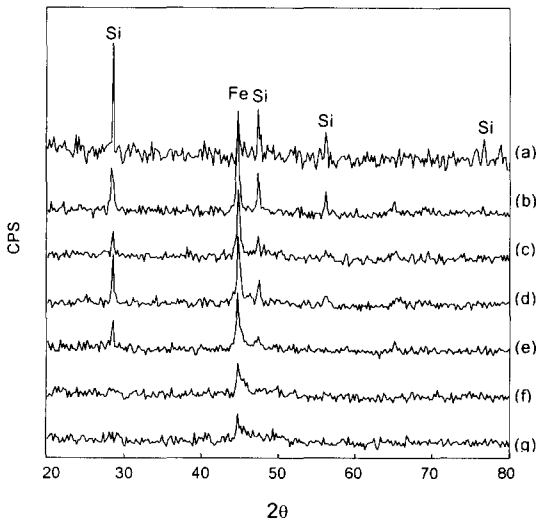

Fig. 3. XRD patterns of the n-type $Fe_{0.98}Co_{0.02}Si_2$ powders fabricated by mechanical alloying; (a) 0hr, (b) 10hrs, (c) 24 hrs, (d) 36hrs, (e) 48 hrs, (f) 72hrs, (g) 100hrs.

um hot pressing(VHP). As-VHPed specimens were nearly fully dense(4.85g/cc), free from cracks but some voids were unavoidable as shown in Fig. 2. XRD analysis as function of milling time is presented in Fig. 3. Though the elemental Si peaks disappeared after 72 hours of milling, the typical alloying development during MA[13], which generally showed the appearance of a superlattice line with decreasing elemental powder peaks during MA process, was not observed in this process. This could be due to the inherently slower rate of phase transformation[6], which led to process for at least 500 hours of milling to induce β-$FeSi_2$ transformation.[14] The presence of Co can not be detectable in Fig. 3, due to their low volume fraction and fine dispersion throughout the matrix.

The iron-silicide compact after vacuum hot pressing at 1000 ℃ and 35 MPa is shown to consist of partially transformed β-$FeSi_2$, and untransformed mixture of α-Fe_2Si_5 and ε-FeSi, as shown in Fig. 4, which is different from the counterparts processed by conventional technology.[6] DTA analysis has been carried out to determine transformation temperature and to apply to subsequent isothermal annealing for the full β transformation. On heating to 1100 ℃, a distinct endothermic peak is seen at 998 ℃ as shown in Fig. 5. This temperature is believed to indicate the peritectoid temperature (α-Fe_2Si_5 + ε-FeSi → β-$FeSi_2$)[15], which is so called "high temperature transformation" temperature(995℃).[16~18] However, on cooling, the peak is no longer observed but an exothermic peak is appeared at 858 ℃ instead. This is believed to indicate the "low temperature transformation" temperature(865 ℃), below which primary transformation of "α-Fe_2Si_5 + ε-FeSi → β-$FeSi_2$" and secondary transformation of "Si + ε-FeSi → β-$FeSi_2$" are taken place in iron silicides.[16~18] Thus, subsequent isothermal annealing has been carried out to induce the low temperature transformation in vacuum at 830 ℃ for 24 hours to provide enough time for diffusion. The XRD analysis after the isothermal annealing resulted in

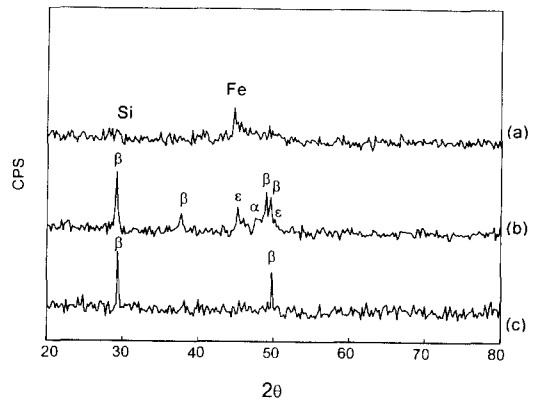

Fig. 4. XRD patterns of $Fe_{0.98}Co_{0.02}Si_2$ powders and compacts; (a) mechanical alloyed for 100hrs, (b) vacuum hot pressed under 35MPa at 1000℃ for 2hrs, (c) vacuum annealed at 830℃ for 24hrs.

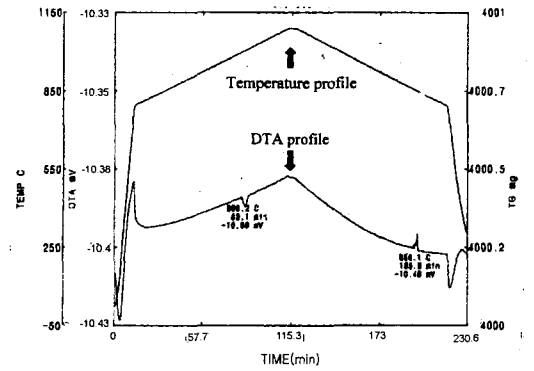

Fig. 5. DTA analysis of the vacuum hot pressed $Fe_{0.98}Co_{0.02}Si_2$ compacts, heated with 60 ℃/min up to 800 ℃ and then heated with 3 ℃/min up to 1100 ℃.

Fig. 6. TEM micrograph of the $Fe_{0.98}Co_{0.02}Si_2$ compacts, showing fully transformed β-$FeSi_2$ after isothermal annealing.

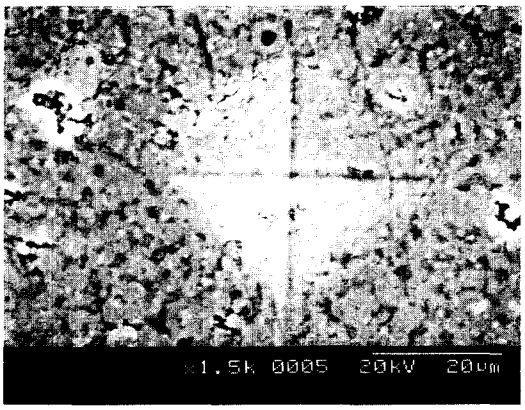

Fig. 7. SEM micrograph of the cracks formed around Hv indents in the vacuum hot pressed $Fe_{0.98}Co_{0.02}Si_2$.

the fully transformed β-$FeSi_2$, as shown in Fig. 4. TEM observation indicated that the microstructure after isothermal annealing is typically fine grained with a grain size of 2 μm, as shown in Fig. 6, and EDS analysis along with XRD analysis revealed that residual α and ε phases were fully transformed to β-$FeSi_2$ during annealing.

The result of microhardness measurements in as-VHPed $Fe_{0.98}Co_{0.02}Si_2$ was Hv 489 and increased to Hv 514 after isothermal annealing, indicating that mechanical properties were improved presumably due to the phase stabilization or the additional sintering effect. It was observed that cracks formed around the microhardness indents, indicating intergranular fracture, as shown in Fig. 7, differently from most ceramic materials which generally showed the crack development from corners.

Thermoelectric and electronic transport properties were evaluated for the as-VHPed and isothermal annealed $Fe_{0.98}Co_{0.02}Si_2$, and their results were shown in Table 1. Electrical conductivity was decreased by annealing treatment because the metallic phases ε and α were transformed to semiconducting phase β, as shown in Fig. 4. Seebeck coefficient was increased by annealing and this was for the same reason - β phase transformation. Seebeck coefficient is inversely related with carrier concentration and electrical conductivity. Electron concentration and mobility changes, which were directly related with electrical conductivity, can be explained by following several reasons: homogenization of Co dopants, their substitution with Fe atoms, β phase transformation, reduction in lattice defects such as vacancies, antistructure defects and so forth. Thermoelectric power factor, which is the measure of thermoelectric material parameters as mentioned above, was also improved by annealing.

4. Conclusion

Iron-silicide was successfully produced by mechanical alloying process and consolidated by vacuum hot pressing. As-consolidated iron silicides were shown to consist of β-$FeSi_2$ and untransformed mixture of α-Fe_2Si_5 and ε-FeSi phases. Subsequent isothermal annealing in vacuum below the critical temperature for 24 hours resulted in thermoelectric semiconducting β-$FeSi_2$ phase transformation. The mechanical properties were improved during isothermal annealing presumably due to the phase stabilization or the additional sintering effect. Thermoelectric properties of iron-silicide materials were also remarkably improved during isothermal annealing due to β phase transformation.

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